Pestic. Sci. 1998, **54**, 121–130

Modelling Pesticide Run-Off to Surface Waters. Part II: Model Application

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(Received 2 March 1998; revised version received 4 June 1998; accepted 3 July 1998)

Abstract: A conceptual model of pesticide run-off to surface water from agricultural land has been tested against data collected from a catchment study. In general the model was able to simulate total run-off and pesticide loss and peak pesticide concentrations to an acceptable level (much better than an order of magnitude) for a number of pesticides in run-off events over five seasons. Hour-by-hour variations in pesticide run-off were reasonably well estimated, although the timing of the estimated peak in pesticide concentrations was always in advance of that observed. A simple sensitivity test of the model showed the sorption coefficients and half-lives of the chemicals simulated were important in controlling model outputs, although the impact of the latter was reduced if events occurred soon after application. Other important parameters were the extent of the enhanced conductivity area above the drains and the parameters controlling the rate of flow of water between the model boxes. © 1998 Society of Chemical Industry

Pestic. Sci., **54**, 121–130 (1998)

Key words: mathematical model; pesticide; surface water; bypass flow; agriculture

1 INTRODUCTION

A conceptual model aimed at predicting short-term pesticide concentrations in surface waters arising from rainfall events has been described in a companion paper.[1] It is important that any model is tested against observed data from sites representative of the conditions under which the model might be expected to be used. In this case, the model is designed to estimate pesticide run-off from agricultural land. A suitable data set for testing was available for a small catchment in Herefordshire, UK which was within the confines of ADAS Rosemaund, an agricultural research facility. In this paper, model outputs are compared to those measured during a five-year monitoring programme.[2–4] The research programme that generated these data contained within it additional information that helped to define not only the conceptualization of the model, but also several of the model parameters. It is therefore an excellent data set on which to conduct an initial test of the model performance for a number of pesticides over a range of hydrological conditions. Ideally, applications of the model to other catchment data sets would be required to perform an independent test.

In addition to testing the model against observed data it is important to know about the sensitivity of model outputs to variations in input parameters. A simple approach to sensitivity analysis is presented in order to assess this, based on two run-off events under contrasting hydrological conditions. Such information is not only useful in the context of the current application, but helps in determining the emphasis on parameter estimation in future applications.

Contract/grant sponsor: National River Authority (Environment Agency).
Contract/grant sponsor: National Environment Research Council.

2 MODEL APPLICATION

2.1 Experimental data

The experimental data that were used to test the model were obtained over five cropping seasons (November

TABLE 1
Values of the Box Thickness (Depth), Moisture Volume Fraction Equivalent to Minimum Water Content (*SMIN*), Field Capacity (*SFC*) and Saturation (*SMAX*), used in the Model, together with the Bulk Density and Organic Carbon Content

Box No.	*Depth* (*mm*)	*SMIN*	*SFC*	*SMAX*	*Bulk Density* ($g\ cm^{-3}$)	*Organic carbon* (%)
1 and 5	0–50	0·19	0·27	0·42	1·21	1·7
2 and 6	50–500	0·24	0·32	0·40	1·42	0·9
3	500–1000	0·30	0·35	0·38	1·38	0·5
4	1000–2000	0·24	0·25	0·26	1·38	0·5
7	500–1000	0·30	0·25	0·40	1·38	0·5

1987–March 1993) from experimental catchments established at ADAS Rosemaund.[2–4] Four nested catchments were used: two were sited on the stream (151 ha and 35·5 ha, referred to as sites 0 and 1) and the two others at the outlets from field drainage systems (5·3 ha and 2 ha, referred to as sites 3 and 5). The soils at Rosemaund are predominantly silty clay loam in texture, predominantly from the Bromyard series, but with Compton and Middleton series also represented in the valley bottoms. These soils are prone to seasonal water-logging and consequently nearly all the fields at Rosemaund are drained, (typically 1 m depth, 20 m spacing). During the summer the soils can crack and these cracks may persist at depth through part or all of the drainage period. There are also macropores extending to depth, and voids around soil peds due to the very blocky nature of the soil structure in the lower parts of the profile.

The monitoring strategy adopted was designed to measure pesticide concentrations in the stream resulting from rainfall events falling on recently treated fields within the catchment. Automatic sampler systems were used to take a series of water samples at short intervals (usually one hour, but intervals of half an hour and four hours were also used) over the duration of rainfall events. In order that these concentrations could be linked to the hydrological response of the catchment, flow was measured at each of the monitoring sites. Rainfall and parameters to estimate potential evaporation were measured hourly by an automatic weather station.

2.2 Selection of model parameters

A complete list and description of the model parameters is given in Part 1 of this paper.[1] The general approach was to assign values to the parameters from measured or literature data. Where this was not possible because of the conceptual nature of the model, values were estimated by calibration against observed data.

The values used for the minimum water content, *SMIN*, the saturated water content, *SMAX* and the field capacity, *SFC* of each soil box are given in Table 1. These were based on observations of water content and soil water potential made in one of the fields in the Rosemaund catchment.[5] The organic carbon content and bulk density of the soil in each of the model boxes was estimated from soil profile analyses carried out by the Soil Survey and Land Research Centre[6] (Table 1). The soil profiles also gave indications of the percentage of macropores, old root channels and fine and severe cracking at a range of depths. These were used to estimate the macropore fractions in each of the model boxes (Table 2). The parameters controlling the movement of water between the boxes representing the different hydrological compartments (i.e. those parameters broadly equivalent to the vertical and horizontal unsaturated and saturated hydraulic conductivities) were obtained by calibration. Measured saturated hydraulic conductivities were available for four sites within one of the fields at ADAS Rosemaund (Table 3).[6] Unfortunately, the sites were selected to identify differences between the shallow and normal soil phases within the Bromyard series rather than located relative to the sub-surface drainage arms. Therefore, these data were most useful for estimating vertical changes in the model parameters equivalent to hydraulic conductivity.

TABLE 2
Values of the Parameters in the Model that are broadly equivalent to Vertical and Horizontal Conductivity and Macropore Extent (*CF*)

	Conductivity ($mm\ h^{-1}$)		*Saturated conductivity* ($mm\ h^{-1}$)		
Box No.	*Vertical*	*Horizontal*	*Vertical*	*Horizontal*	*CF*
1	0·01	0·01	0·1	0·1	0·02
2	0·001	0·001	0·005	0·005	0·05
3	0·001	0·001	0·005	0·005	0·02
4	0·0	0·0002	0·0	0·0004	0·01
5	1·0	0·20	2·0	0·2	0·02
6	1·0	0·20	2·0	0·2	0·05
7	0·1	0·20	0·4	0·2	0·02

TABLE 3
Saturated Vertical Hydraulic Conductivities (mm h^{-1}) measured at Four Sites at ADAS Rosemaund.

Depth (mm)	*Site 1A*	*Site 1B*	*Site 2A*	*Site 2B*
0–300	35·8	11·7	4·2	2·1
300–450	28·8	12·9	3·3	2·5
450–600	37·1	11·3	0·8	1·7
600–800	3·3	2·9	1·7	1·2

Sites 1 and 2 were on the shallow and normal phases of the Bromyard soil series respectively. Values shown are the average of two to four measurements at each site.

The observed data showed a large variation in values between the Bromyard soil phases and a much lesser variation within a given soil phase. In both soil phases saturated vertical conductivities were similar over the top 450 mm. In the Bromyard normal phase there was then a marked drop in conductivities below this depth. In the Bromyard shallow phase this drop did not occur until 600 mm. This pattern, together with the results of the soil water movement study,[5] were used to help set the values for the initial estimates of the model vertical saturated hydraulic conductivities. Some modifications to the values were required because, within the model, the driving force for water movement from a box is the excess of the water content over the minimum water content, and the size of the box will therefore influence the value of the conductivity parameter. There is, therefore, some scope for using measurements of saturated conductivity to help in setting these parameter values within the model. The initial calibration involved setting values which resulted in drain flow of the correct magnitude beginning at the correct time and was based on observed data from one of the field drain outlets (site 5) for the 1992/1993 season. The model was then tested against flow data from the outlet from the whole catchment (site 0) for the same season. The values for the parameters used are given in Table 2. The base flow rate was set at 4·0 litre s^{-1}, estimated from the observed flow leaving the catchment in early autumn.

The model was driven by hourly rainfall and daily estimates of potential evaporation according to the method of Penman.[7] The model was used to simulate concentrations of the pesticides isoproturon, lindane, simazine, mecoprop, trifluralin and dichlorprop leaving both field drains and at both stream monitoring sites. Parameters for the six pesticides are given in Table 4. The applications were made to crops as part of their normal use on the farm, using a tractor-mounted sprayer, subsequently updated to a self-propelled unit from spring 1990. For each pesticide for each season in which it was studied, the application rates were taken from records kept by staff at ADAS Rosemaund (see Table 6). Values of the organic carbon partition coefficients, k_{oc} and degradation rates were obtained from the literature or from data collected during the field experiments.

TABLE 4
Physicochemical Properties of the Pesticides used in the Model Simulations

Chemical	k_{oc}[a] *(litre kg*$^{-1}$*)*	*Half-life*[a] *(days)*
Isoproturon	130[b]	20[c]
Lindane	1100	400
Simazine	130	60
Mecoprop	7[d]	21
Dichlorprop	1000	10
Trifluralin	8000	60

[a] Reference 12.
[b] D N Brooke, pers comm.
[c] Fitted from Rosemaund data.
[d] Reference 13.

3 RESULTS AND DISCUSSION

3.1 Model performance

When applying a pesticide run-off model, it is necessary to ensure that the movement of water is adequately modelled and that this part of the assessment is made first.[8] The potential evaporation is assumed to equal the actual evaporation whenever there is sufficient water available to meet the demand.

It is clear from Fig. 1 that the model was able to represent the patterns of flow from the catchment very well. However, the highest peaks were underestimated by the model while the fall back to base flow conditions was predicted to occur too quickly. This resulted in a substantial underestimate in the volume of water leaving the catchment—11·8 mm predicted over the period 1 October 1992 to 8 December 1992 compared to an observed total of 22·5 mm. This was at least partly due to an overestimate of the observed flows caused by backing up of the water below the weir, which under high flows drowned out the weir. Stream flow was estimated using a theoretical relationship between stream level above the weir assuming free movement of water away from the downstream side of the weir. When the weir was drowned out, the theoretical relationship no longer held. The result was that levels upstream of the weir were made higher for a given flow rate and were maintained at a higher level for longer after rainfall had ceased. However, the shape of the simulated hydrograph was very similar to the observed data for all of the storm events. In the second half of the simulation there was good agreement between the modelled and measured decline in river flows to base flow conditions. Observed data on the

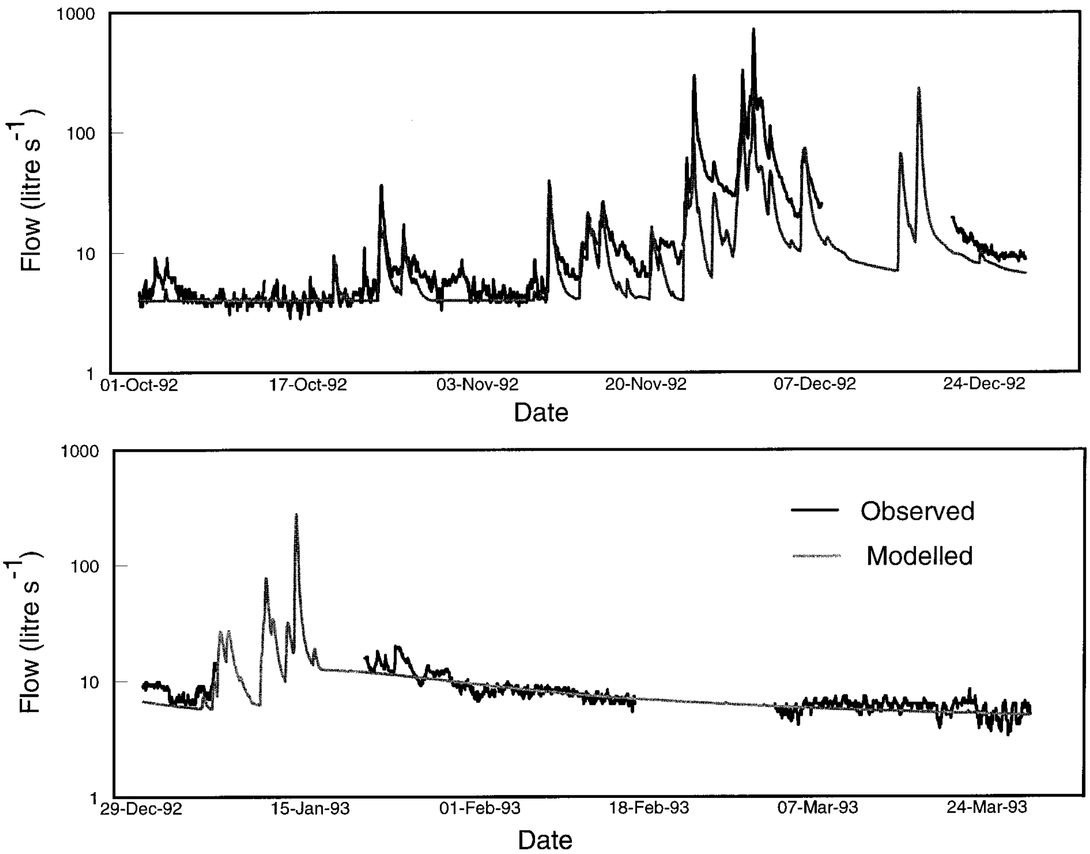

Fig. 1. Modelled and observed flow at the outlet from the ADAS Rosemaund catchment from September 1992 to March 1993.

occurrence of overland flow were compared to the occasions on which the model predicted this to occur for the 1990/91 season (Table 5).[5] The model generated overland flow less often than it was observed within the single instrumented 1-m^2 plot for which data were available. The model required large amounts of rainfall in one event or consecutive events to generate overland flow. The field in which the plot was located had a slope of 6%, almost twice the value used in the model for the catchment as a whole. Therefore, it is not surprising that this field might generate overland flow more often than predicted for the whole catchment.

The model parameters obtained by calibration to drain flow were kept constant for all simulations. The sampling programme at ADAS Rosemaund was event-based, with many samples taken over short time-periods during each of the seasons studied. There were many observed events against which to compare the model output. From these, two contrasting events within a single season have been chosen to illustrate the model performance in detail for the herbicide simazine. The event of 25 December 1990 was the first major run-off event of the season, which occurred particularly late in the year, 32 days after the pesticide application of 4·3 kg of simazine on 23 November 1990. This event therefore combined a long time-lag from application with the difficulties which might arise from modelling the first substantial run-off event of the season. The

TABLE 5
Comparison between Observed and Modelled Predictions of Occurrences of Overland Flow for Selected Events during the 1990/91 Season

Data	*Rainfall (mm)*	*Overland flow generation*	
		Observed	*Modelled*
19 November 1990	6·5	Yes	No
23 November 1990	9·5	Yes	No
24 November 1990	4·0	Yes	Yes
9 December 1990	3·0	Yes	No
20 December 1990	5·5	Yes	No
25 December 1990	17·5	Yes	Yes
5 January 1991	6·0	Yes	No
8 January 1991	17·5	Yes	Yes
9 January 1991	6·0	Yes	Yes
15 March 1991	1·0	No	No
16 March 1991	9·0	Yes	No
17 March 1991	5·0	No	No
18 March 1991	5·0	No	No
20 March 1991	3·5	No	No
22 March 1991	0·5	No	No
2 April 1991	7·0	No	No
4 April 1991	9·5	Yes	No
6 April 1991	4·5	No	No

event of 16 March 1991 occurred 113 days after the application described above, but only two or three days after a second simazine application of 2·2 kg to different fields. This second application occurred at a time of year when the catchment was relatively wet at depth, but some drying had occurred near the surface. Figure 2 shows the results of the model simulations for the December event. At this short temporal scale it is clear that the modelled flow peaked an hour earlier and at almost twice the magnitude of the observed data. Overall, the modelled run-off total of 3·6 mm was some five times that of the observed (0·7 mm). The simazine simulations were similar to the flow simulations, with the peak value occurring at the correct time but at twice the magnitude. The estimated mass of pesticide leaving the catchment was overestimated at 7·5 g compared to 1·8 g calculated from the observed data. This is a similar ratio to that for the run-off estimates. The fall from the peak value was similar in both the simulated and the observed concentrations. It is interesting to note that the model predicted elevated increased concentrations in the period before samples were taken

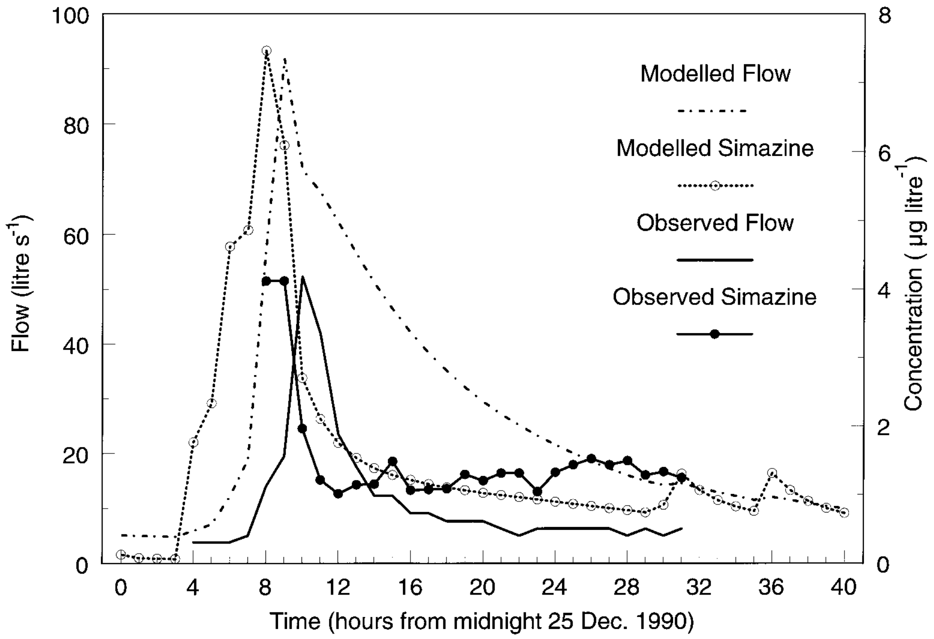

Fig. 2. Modelled and observed flow and simazine concentrations at the outflow from the Rosemaund catchment during a rainfall event on 25 December 1990.

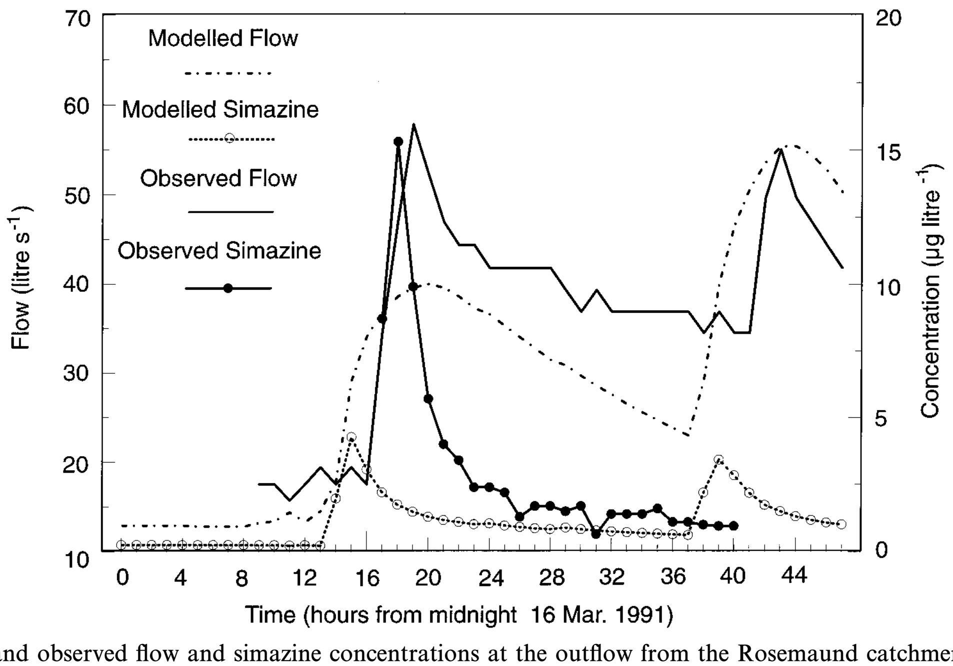

Fig. 3. Modelled and observed flow and simazine concentrations at the outflow from the Rosemaund catchment during a rainfall event on 16–17 March 1991.

from the stream. Similar information is given for the March event in Fig. 3. Here, with the catchment wetter, the simulated hydrograph was in better agreement with the observed data, with the modelled run-off over the event 1·9 mm compared to 2·3 mm calculated from the observed data. On this occasion the peak simazine concentration was underestimated by a factor of about 4 and the timing of the peak was some three hours in advance of the observed peak. The model predicted a pesticide loss of 3·3 g of simazine during the event compared to 11·8 g calculated from the observed data. The underestimation of the peak simazine concentration may, in part, be explained by the proximity to the stream monitoring point of the sites receiving a second application two or three days before the event. In the model, run-off in a given hour from treated fields will be diluted instantaneously by mixing within the stream with water from untreated fields in the rest of the catchment. In reality, water from fields closer to the monitoring site will arrive first and any pesticide associated with this water will not be subjected to as much dilution as assumed in the model. However, the Rosemaund catchment responds quickly to rainfall and this explanation should only be valid for, perhaps, the first two hours of an event.

The results of all the model simulations carried out for events monitored at ADAS Rosemaund are summarized by pesticide in chronological order for each monitoring site in Table 6. Comparisons are made between observed and modelled data in terms of the total run-off, total pesticide loss, peak pesticide concentration and the error in the prediction of the timing of the pesticide peak. The model produced good estimates of total run-off and pesticide losses, generally better than in the contrasting events discussed above. In all but one case the estimates of peak pesticide concentration were within one order of magnitude of the measured values and often much better estimates were made. A bias of two to one in favour of overestimating observed values was evident from the data, although this seemed not to be related to either the pesticide or the sampling point. The time of the peak concentration was generally not predicted well and the modelled peak always anticipated the observed peak by several hours. In several cases this was due to an observed time series that did not show a simple response of the kind seen in Figs 2 and 3. Rather, the observed pesticide concentration showed either several peaks or little relationship to run-off at all. Compounds with a range of physicochemical properties were used in the model testing (Table 4). It is of particular interest that the model predicted concentrations of trifluralin, which is highly sorbed ($k_{oc} = 8000$ litre kg^{-1}), at least as well as for any of the other compounds that were simulated. The other highly sorbed chemical studied was lindane ($k_{oc} = 1100$) and the model simulated the observed concentrations well in two of the four events studied. Simulations of isoproturon II ($k_{oc} = 130$) concentrations for the same event give an interesting contrast. The model generally overestimated the isoproturon values. For the events at site 1 on 13 December 1989 and site 3 on 8 November 1989 this was probably due to missing samples from the initial part of the run-off event due to automatic-sampler failure.[9] Events at ADAS Rosemaund have previously been shown to have initially high pesticide concentrations that fall rapidly within hours of the start of the hydrograph.[2–4] The overestimate of isoproturon is consistent with the model simulations for lindane given the difference in the sorption properties of the chemicals (as would be expected since these are explicitly modelled). It follows that lindane appears to have run off in larger amounts than may have been expected compared with the isoproturon values. However, this is probably explicable in terms of underestimating the isoproturon run-off due to the automatic-sampler failure described above.

Other modelling approaches to estimating pesticide run-off which have been applied to the Rosemaund catchment data are the SoilFug[10] and SWAT[11] models. These approaches were aimed at predicting the mean and peak pesticide concentrations, respectively, associated with a run-off event, but make no attempt to model the run-off event in detail. The estimates made of the mean and peak pesticide concentrations by these models were generally better than one order of magnitude and are therefore of the same order as the estimates made using the model results presented in this paper. The advantage of the model presented here is that since it simulates at an hourly time step, it can provide information on the duration of pesticide run-off events. The observed event data were not sufficient to demonstrate convincingly that the model adequately estimated duration of events. However, Figs 2 and 3 show a reasonable similarity between model and predicted event durations, which at least indicates some functionality of the model in this respect.

3.2 Sensitivity testing

Sensitivity testing was carried out to allow some estimate of the importance, expressed in terms of the effect on model output, of the model parameters used, both relatively and in absolute terms. Relative importance allows intelligent selection of input parameters, concentrating most effort on those parameters that have the most effect. Absolute importance is similar, but the purpose is to identify parameters where uncertainty in their value is magnified through the modelling process. The approach to sensitivity testing adopted here is simple, but still allows this information to be obtained.

Each of the model parameters has been subjected to increases and decreases in its value in line with the degree of uncertainty that might be expected for that

TABLE 6
Summary of the Results of the Simulation of Pesticide Transport at ADAS Rosemaund for a Number of Rainfall Events

Pesticide	*Site No.*	*Amount applied (kg)*	*Date of event*	*Days from application*	*Rainfall amount (mm)*	*Total run-off (mm)*		*Total pesticide loss (g)*		*Obs. max. (μg litre^{-1})*	*Predicted max. (μg litre^{-1})*	*Time error (h)*
						Obs.	*Predicted*	*Obs.*	*Predicted*			
Isoproturon	1	6/3·75	13/12/89	45/27	54	4·3	4·9	3·8	5·8	5·4	15·1	12
	3	2·1	8/11/89	8	28·5	1·0	5·2	0·1	0·4	8·4	20·2	6
	3		10/11/89	10	10·5	0·4	2·7	0·1	0·2	13·7	11·4	8
	3		13/12/89	45	54	4·7	8·7	0·7	0·5	8·8	16·5	9
	0	13·8/23·4/5·2	25/12/90	75/44/32	17·5	0·7	3·3	0·6	8·9	1·8	6·7	13
	0		5/01/91	86/55/43	9·5	1·3	1·4	0·7	2·0	5·2	1·8	20
	0		8/01/91	89/58/46	20	—[a]	4·9		6·6	6·7	2·1	20
	0		21/02/91	132/101/89	11·5	2·8	2·3	BDL[b]	0·5	<0·02	0·2	—
	1	10·8/11·1	25/12/90	72/33	17·5	0·3	0·9	1·0	2·4	17·2	17·0	1
	1		8/01/91	86/47	20	1·3	2·9	0·5	1·7	2·6	4·3	3
	1		21/02/91	132/93	11·5	1·3	1·4	0·4	0·1	2·1	0·3	2
	5	4·2	21/02/91	91	11·5	2·8	2·9	$7·5 \times 10^{-2}$	$7·5 \times 10^{-2}$	2·6	1·5	6
	5		4/03/91	113	13·5	2·8	2·5	$8·0 \times 10^{-2}$	$5·0 \times 10^{-2}$	2·5	0·9	24
Lindane	1	3·4	13/12/89	45	54	4·3	4·9	0·1	1·1	0·3	2·9	10
	3	1·2	8/11/89	6	28·5	1·0	5·2	$6·5 \times 10^{-2}$	$7·5 \times 10^{-2}$	4·5	3·6	6
	3		10/11/89	8	10·5	0·4	2·7	$2·8 \times 10^{-2}$	$4·2 \times 10^{-2}$	4·1	3·6	5
	3		13/12/89	43	54	4·7	8·7	$3·5 \times 10^{-2}$	0·12	0·5	3·0	7
Simazine	0	6·9/7/6·4	24/02/89	79/9/8	13·5	1·4	1·3	58·3	71·9	68·0	90·1	3
	0		2/03/89	79/9/8	10·5	0·8	0·2	9·8	2·2	15·7	27·2	8
	1	5·75	24/02/89	79	13·5	3·9	0·5	0·3	1·6	1·8	20·4	12
	0	4·5	25/12/90	32	10·5	0·7	3·6	1·8	7·5	4·1	7·5	1
	0		5/01/91	43	9·5	1·3	1·4	1·7	2·0	1·5	2·1	7
	0		8/01/91	46	20·5	—	4·9	—	7·7	0·7	2·8	1
	0		21/2/91	90	11·5	2·9	2·3	1·1	1·9	0·4	0·8	4
	0	4·5/1·2/1	16/03/91	113/3/2	9·5	2·3	1·9	11·8	3·3	15·3	4·3	3
Mecoprop	1	10·4	15/5/90	55	12	0·2	0·4	$1·5 \times 10^{-2}$	$0·8 \times 10^{-2}$	1·4	3·0	16
Dichlorprop	1	41·6	15/5/90	55	12	0·2	0·4	$1·8 \times 10^{-2}$	$1·2 \times 10^{-2}$	1·0	0·6	14
Trifluralin	5	2·2	11/11/90	5	11·5	1·1	2·6	$5·3 \times 10^{-3}$	$8·0 \times 10^{-3}$	14·1	1·9	2
	5		15/11/90	9	9	1·4	1·1	$1·5 \times 10^{-2}$	$0·2 \times 10^{-2}$	2·2	0·4	1

[a] —: No flow data available.
[b] BDL: below detection limit.

parameter. Corresponding changes in model estimates of total pesticide loss and maximum pesticide concentrations have been quantified as a percentage change relative to the prediction arising from the original model estimate. This procedure was carried out for the two simazine run-off events described above. The results from the sensitivity testing for those parameters in the model that relate to the flow of water[1] are given in Table 7. Model predictions were most sensitive to the parameter setting the proportion of the catchment that could be considered to be acting as a high conductivity area (HCA). Increasing this fraction increased the loss of pesticide predicted in the stream for both the December and March events by more than the increase in the parameter value. The increase was due to increased amounts of water reaching the stream during the events. The effect on concentration was less marked and was only significant for the March event which occurred sooner after the pesticide application. As less degradation was likely to have taken place, more pesticide would be available to travel by the newly increased rapid route. Decreasing the fraction considered to be of high conductivity caused a corresponding decrease in pesticide concentrations. Other than in this case, none of the changes in parameter magnitude gave rise to a greater change (in percentage terms) in either the predicted pesticide losses or maximum concentrations in either run-off event. Errors in the accuracy with which individual parameters are known will not therefore be magnified though the modelling process; in fact, in most cases, such errors will, to some extent, be ameliorated. However, only single parameter errors have been considered here, whereas, in reality, there is likely to be an error associated with each parameter. These errors may either be additive to produce a greater model error than indicated above (likely) or, by chance, may be of opposite sign leading to a reduced error (unlikely). In either case, it is important to consider the interaction between parameters when applying this or any model.

Increasing the horizontal conductivity parameters ($SATkh_{1-7}$) was the only other significant change with respect to the change in the parameter value. The effect was greater for the December event than for the March event, indicating that the model predicts an increased contribution of lateral flow to the stream flow early in the drainage season (the first drain flow was not initiated until soon before this event). Perhaps most interesting was the insensitivity of the model outputs to changes in the parameters describing the extent of macropores through the soil profile (CF_i). This implies that in this model conceptualization it is not necessary to consider macropores explicitly because they are assumed implicitly by the introduction of the high conductivity zone above the drains. In this zone, the large value for the vertical saturated conductivity parameter ($SATkv_{5-7}$) effectively allows rapid flow from the surface layers to the layers feeding the drains under saturated or near saturated conditions.

The model predictions were also sensitive to those parameters related to the physicochemical properties of the pesticide (Table 8). This is because the half-life and sorption coefficient effectively determine how much of the pesticide is available for transport. This sensitivity is important because measurements of these parameters reported in the literature clearly show variations similar to those used in this sensitivity analysis.[12] Increasing

TABLE 7

Sensitivity of Model Estimates of Simazine Loss and Maximum Concentrations to Variations in hydrological Parameter Values

Parameters	Change	*Change in total pesticide loss* (%)		*Change in the maximum concentration* (%)	
		25 Dec. 1990	*16 Mar. 1991*	*25 Dec. 1990*	*16 Mar. 1991*
$SMAX_4$	+10%	−4·6	−0·6	+1·9	+2·9
$SATkh_4$	×10	−4·1	−0·5	−0·4	−0·2
$SATkh_4$	×0·1	+0·3	0·0	−15·3	−0·2
$SATkv_{1-3}$	×10	−63·6	−60·0	−57·3	−19·8
$SATkv_{1-3}$	×0·1	+36·5	+53·9	−0·8	+37·1
$SATkh_{1-3}$	×10	+272·3	+124·8	+25·9	+76·2
$SATkh_{1-3}$	×0·1	−46·4	−49·7	−14·8	−16·2
$SATkv_{5-7}$	×10	−62·3	−37·5	−77·5	−62·4
$SATkv_{5-7}$	×0·1	+87·4	+1·1	+52·0	+1·0
$SATkh_{5-7}$	×10	+145·5	+30·3	+28·0	+60·2
CF_{1-4}	Double number of macropores	+0·4	+7·5	+2·8	+0·5
CF_{5-7}	Double number of macropores	+2·1	+2·5	+7·1	−0·5
CF_{1-4}	No macropores in slow flow zone	+5·2	+7·1	−1·0	+3·0
CF_{1-7}	No macropores in any box	+4·0	+7·8	−1·0	+6·0
HCA	+100·0	+102·8	+111·1	−8·1	+31·4
HCA	−50·0	−51·8	−51·1	−6·7	−17·5

TABLE 8
Sensitivity of Model Estimates of Simazine Loss and Maximum Concentrations to Variations in Pesticide Half-Life and Soil Sorption

Model parameter	*Change* (%)	*Simazine event date*	*Change in pesticide loss* (%)	*Change in maximum concentration* (%)
K_{oc}	−50	25 December 1990	+55·3	+21·2
		16 March 1991	+55·2	+64·0
	+100	25 December 1990	−41·5	−47·3
		16 March 1991	−41·8	−41·7
Half-life	−50	25 December 1990	−35·8	−45·6
		5 January 1991	−44·0	−44·3
		8 January 1991	−47·5	−47·1
		21 February 1991	−71·6	−72·5
		16 March 1991	−24·3	−9·5
	+100	25 December 1990	+24·9	+5·5
		5 January 1991	+37·5	+36·2
		8 January 1991	+37·4	+37·1
		21 February 1991	+89·5	+80·0
		16 March 1991	+34·4	+11·7

the sorption coefficient decreases the amount of pesticide in solution and therefore reduces the concentration in the stream. Decreasing the sorption coefficient has the opposite effect. Variability in the value of the degradation half-life had an effect on model predictions that becomes greater the longer the interval between the application date and the event of interest. This effect is clearly seen in Table 8 where data on all five run-off events following simazine application are shown. The March event shows the least change in model output due to the close proximity of this event to a second simazine application.

Clearly the model is sensitive to a small range of parameters, although, in general, the sensitivity displayed by the model is less than the variation imposed on the parameter values. Those parameters that need to be known well are the extent of the high conductivity area and the properties of the pesticide. The former requires some knowledge of the extent of drainage within the catchment, which may be available from the original drainage plans or from local knowledge. Pesticide properties are certainly best measured using soil samples collected for the catchment being studied. As a first estimate, the parameters could be extracted from appropriate reference works.[13]

4 CONCLUSIONS

A pesticide run-off model has been tested against observed data collected as part of a pesticide run-off study at ADAS Rosemaund. The model provided good estimates of observed data (within an order of magnitude) for both the total pesticide loss and peak pesticide concentrations occurring in individual rainfall events. The model, therefore, provides the basis of a tool for estimating pesticide loss from agricultural catchments to surface waters. However, the model has been applied to only one catchment and the transferability to other catchments would need to be proven before it could be considered for wider use.

ACKNOWLEDGEMENTS

The funding for this work was provided by the National Rivers Authority (now part of the Environment Agency) and the Natural Environment Research Council whose support is gratefully acknowledged. The author would also like to thank the Centre for Environment, Fisheries and Aquaculture Science laboratory at Burnham-on-Crouch for allowing the use of their data in Table 4 and the staff at ADAS Rosemaund for providing the pesticide application data.

REFERENCES

1. Williams, R. J., Modelling pesticide run-off to surface waters, Part I: Model theory and development, *Pestic. Sci.*, **54** (1998) 113–120.
2. Williams, R. J., Bird., S. C. & Clare, R. W., Simazine concentrations in a stream draining an agricultural catchment. *J. IWEM*, **6** (1991) 80–84.
3. Matthiessen, P., Allchin, C., Williams, R. J., Bird, S. C., Brooke, D. & Glendinning, P. J., The translocation of some herbicides between soil and water in a small catchment. *J. IWEM*, **6** (1992) 496–504.
4. Williams, R. J., Brooke, D. N., Matthiessen, P., Mills, M., Turnbull, A. & Harrison, R. M., Pesticide transport to surface waters within an agricultural catchment. *J. IWEM*, **9** (1995) 72–81.

5. Bell. J. P., Abbott, C. L. & Batchelor, C. H., The Soil hydrology of 'Longlands', ADAS Rosemaund, Herefordshire: Second Interim Report—Crop Year 1990/91. In *Pesticide Runoff Study at Rosemaund*, *Report of Years 2 to 5*, ed. C. M. Hack. ADAS, Oxford, UK, 1994.
6. Carter, A. D. & Beard, G. R., Interim report on the soil water sampling and soil characterization programme within a small catchment at Rosemaund EHF (1990–1991). Soil Survey and Land Research Centre, Silsoe, Beds., UK, unpublished.
7. Penman, H. L., Natural evaporation from open water, bare soil and grass, *Proc. R. Soc. London*, *Ser. A*., **193** (1948) 120–46.
8. Armstrong, A. C., Portwood, A. M., Leeds-Harrison, P. B., Harris, G. L. & Catt, J. A., The validation of pesticide leaching models, *Pestic. Sci*., **48** (1996) 47–55.
9. Williams, R. J., Brooke, D. N., Glendinning, P. J., Matthiessen, P., Mills, M. J. & Turnbull, A., Measurement and modelling of pesticide residues at Rosemaund Farm. In *Proc. Brighton Crop Prot. Conf.—Weeds*, *1991*, British Crop Protection Council, Farnham, Surrey, **2** (1991) 507–14.
10. DiGaurdo, A., Williams, R. J., Matthiessen, P., Brooke, D. N. & Calamari, D., Simulation of pesticide runoff at Rosemaund Farm (UK) using the SoilFug model. *Environ. Sci. Pollut. Res*., **1** (1994) 151–60.
11. Brown, C. D. & Hollis, J. M., SWAT—A Semi-empirical model to predict concentrations of pesticides entering surface water from agricultural land. *Pestic Sci*., **47** (1996) 41–50.
12. Wauchope, R. D., Buttler, T. M., Hornsby, A. G., Augustin Beckers, P. W. M. & Burt, J. P., The SCS/ARS/CES pesticide properties database for environmental decision making. *Rev. Environ. Contam. Toxicol*., **123** (1992) 1–164.
13. Tomlin, C. (ed.), *The Pesticide Manual*, 10th edn. British Crop Protection Council, Farnham, UK, 1994.